

# PATENT SPECIFICATION

NO DRAWINGS



881,927

Date of filing Complete Specification: May 31, 1960.

Application Date: June 16, 1959.

No. 20670/59.

Complete Specification Published: Nov. 8, 1961.

Index at acceptance:—Class 2(3), C2B43(A1: A3: B1: B3: C1: C3), C3A14A(3A: 7C).

International Classification:—C07c, d.

## COMPLETE SPECIFICATION

### Improvements in or relating to the production of Amides and Lactams

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, and IAN STUART FISHER, of the Company's Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, and of British nationality, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is 5 to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of amides or lactams.

It is known that cyclohexanone oxime is 10 converted to epsilon-caprolactam in the presence of a very large excess of concentrated sulphuric acid. This process has the disadvantage that the caprolactam can only be recovered from the product after neutralisation of this 15 acid. This is usually effected by means of ammonia; although ammonium sulphate is recovered, the neutralisation of acid under these conditions constitutes an economic disadvantage.

A process for the conversion of cyclohexanone oxime to caprolactam has been proposed in which the feedstock, in vapour phase, is passed over boric acid supported on pumice. In contrast, in accordance with the present invention there may be used a cheap and readily 20 available catalyst conventionally employed in cracking reactions.

Furthermore, we have investigated the use 25 of alumina catalysts and silica catalysts for use in this reaction and have found that these catalysts have negligible activity.

According to the present invention an amide or lactam is formed by bringing an oxime, in 30 vapour phase, in contact with a silica/alumina catalyst.

Preferably the silica/alumina catalyst employed is a conventional silica/alumina cracking catalyst.

Preferably the catalyst contains a proportion of silicon, estimated as silica, greater than 5% by weight of the silica/alumina and a proportion of aluminium, estimated as alumina, also greater than 5% by weight. A suitable catalyst contains 12.5% by weight of aluminium, estimated as alumina, and 87.5% by weight of silicon, estimated as silica. 45

Preferably the catalyst is formed by co-precipitation from water-soluble aluminium-containing and silicon-containing compounds. The co-precipitated material will usually be separated, washed, dried and activated by roasting in the presence of air, suitably at 550°C for 5 hours. 50

A preferred class of compound for treatment in accordance with this invention consists of the cycloalkanone oximes. By the use as feedstock of cyclohexanone oxime there is obtained epsilon-caprolactam. 55

Other compounds which may be treated according to this invention are dialkyl ketoximes, diaryl ketoximes and alkyl-aryl ketoximes, alkyl aldoximes and aryl aldoximes. 60

Usually reaction temperatures will lie in the range 130—500°C. Pressure will preferably be below atmospheric; if desired atmospheric or higher pressure may be employed. When using cyclohexanone oxime as feedstock a pressure in the range 0.5—20 cms pressure of mercury is suitable. 65

If desired the oxime may be passed over the catalyst as a mixture with an inert gaseous phase diluent. 70

The reaction may be carried out over a fixed catalyst bed, or over a moving catalyst. If desired a "fluidised" catalyst may be employed. 80

When employing a fixed bed a temperature gradient will be set up due to the exothermic nature of the reaction. Preferably flow rate and applied heat are adjusted to maintain the highest temperature zone in the catalyst bed 85

[Price 3s. 6d.]

in the range 250—350°C. Contact time will be as low as possible consistent with a high level of conversion.

5 Excessive contact time will lead to loss of yield as a result of the greater effect of side-reactions.

10 When employing a "fluidised" catalyst virtually no temperature gradient is established in the reaction zone and overall temperatures may be higher, being preferably in the range 340—400°C. Short contact times are readily achieved thereby largely avoiding the effect of side-reactions. Fluidisation may be achieved by the use of a diluent gas stream 15 or by means of the feedstock in vapour phase or by a combination thereof.

15 The oxime may be used in admixture with a polymerisation inhibitor in order to reduce side reactions involving polymerisation of the amide.

20 This invention is illustrated but not limited by the following Examples.

#### EXAMPLE 1

25 The reactor employed consisted of a vertical glass tube of 4.5 cms internal diameter being 22 cms in length, a sintered glass disc being attached to the lower end. 0.6 grams of catalyst in the form of 44—72 BSS mesh particles was contained in the tube and, in operation, maintained in a fluidised state by means of the feedstock diluted with nitrogen which was passed upwards through the sintered disc. Product was continuously taken from the top of the tube to a cyclone separator for the removal 30 of fines and thence to an air condenser. The system, including feedstock vaporiser, was maintained at reduced pressure by an oil pump attached to the condenser. The reactor tube was fitted with a thermocouple pocket which 35 extended into the centre of the fluidised catalyst bed.

40 The catalyst employed was a silica/alumina cracking catalyst containing 12.5% by weight of alumina and 87.5% by weight of silica.

45 Over a period of 30 minutes, 8.4 grams of pure cyclohexanone oxime was vaporised at 150°C and passed through the reactor, the pressure of the system being such that the pump suction inlet was stabilised at 3mm. of mercury. Nitrogen, at low feed rate was slowly bubbled through the liquid oxime. Reaction 50 temperature as recorded at the thermocouple pocket was 388—390°C.

55 Total solid product recovered was 94% by weight of the oxime feed. Infra-red and spectroscopic analysis of the product showed that 77% by weight of the oxime feed had reacted and the yield of epsilon-caprolactam was 92% by weight of the oxime which had 60 undergone reaction.

#### EXAMPLE 2

The run described in Example 1 was

repeated under modified conditions, as follows.

65 The catalyst charge was 4.7 grams, and the quantity of feedstock vaporised was 8.0 grams. Operating temperature was maintained in the range 340—390°C. and pressure at the pump suction inlet was 3 mms. of mercury.

70 Total solid product recovered was 82% by weight of feed; the conversion of oxime was 99%, by weight and the yield of epsilon-caprolactam was 80% by weight of oxime reacted.

#### EXAMPLE 3

75 The run described in Example 1 was repeated under modified conditions as follows:—

80 The catalyst charge was 0.5 grams, and the quantity of feedstock vaporised was 15 grams. Vaporisation took place over a period of 15 minutes. Operating temperature as measured at the thermocouple pocket lay in the range 380—390°C; the feed temperature at the sintered disc was 360—370°C. Pressure at the pump suction inlet was 30 mms. of mercury.

85 Total solid product recovered was 95% by weight of feed; the conversion of oxime was 83% by weight and the yield of epsilon-caprolactam was 80% by weight of oxime reacted.

#### EXAMPLE 4

90 This example describes the conversion of cyclohexanone oxime to epsilon-caprolactam using a fixed catalyst bed.

95 The reactor consisted of a vertical glass tube of 12 mm internal diameter being 25 cms in length, and contained 2.8 grams of 18—44 BSS mesh silica/alumina cracking catalyst, containing 12.5% by weight of alumina and 87.5% by weight of silica.

100 91.7 grams of cyclohexanone oxime was maintained at 150°C and vaporised over a period of 7 hours in a slow stream of nitrogen. The oxime vapours were passed upward through the reactor and product was condensed in an air-cooled condenser. Catalyst bed temperature was 380—400°C. Pressure at the pump suction inlet was 3 mm.

105 110 Total product recovered was 73% by weight of oxime feed. 79% by weight of the feed had reacted and the yield of epsilon-caprolactam was 56% by weight of the oxime which had reacted.

#### EXAMPLE 5

115 This example illustrates the activity of a silica/alumina catalyst for the conversion of cyclohexanone oxime to epsilon-caprolactam and the inactivity of a silica catalyst and an alumina catalyst under comparable conditions.

120 The method employed was as described in Example 4, conditions being modified as shown in the following Table.

TABLE

Run No.	Catalyst	Catalyst Quantity (grams)	Quantity of feedstock (grams)	Reaction Temperature	Product and Yield % by weight
1	Alumina/silica	14.00	11.21	165—175°C.	caprolactam in 55% crude yield
2	Alumina	11.6	9.6	160—165°C.	No conversion
2a	Alumina	11.6	7.9	225°C.	No conversion
3	Silica	6.1	9.0	150°C.	No conversion
4	Silica	11.6	17.8	170—200°C.	caprolactam 3.8% oxime 85.4%

Run 1 was carried out at a pressure of 4 mm of mercury; Runs 2—4 at a pressure of 15—30 mms of mercury.

**WHAT WE CLAIM IS:—**

1. Process for the production of an amide or lactam which comprises bringing an oxime, in vapour phase, in contact with a silica/alumina catalyst.
2. Process according to claim 1 in which the catalyst contains a proportion of silicon, estimated as silica, greater than 5% by weight of the silica/alumina and a proportion of aluminium, estimated as alumina, also greater than 5% by weight.
3. Process according to claim 1 or 2 in which the catalyst is employed as a fixed bed catalyst.
4. Process according to claim 1 or 2 in which the catalyst is employed as a fluidised catalyst.
5. Process according to any one of the preceding claims in which the oxime is a cyclo-alkanone oxime.
6. Process according to claim 5, for the production of epsilon caprolactam, in which the oxime is cyclohexanone oxime.
7. Process according to any one of the preceding claims in which the reaction temperature lies in the range 130—500°C.
8. Process according to claim 6 in which the reaction pressure lies in the range 0.5—20 cms pressure of mercury.
9. Process for the production of an amide or lactam substantially as described with reference to any of the foregoing Examples.
10. Amides or lactams whenever produced by a process as claimed in any one of the preceding claims.

J. WOOLARD,  
Agent for the Applicants.

**PROVISIONAL SPECIFICATION**

**Improvements in or relating to the production of Amides and Lactams**

We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Finsbury Circus, London, E.C.2, a British joint-stock Corporation, and IAN STUART FISHER, of the Company's Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, and of British nationality, do hereby declare this invention to be described in the following statement:—

This invention relates to a process for the production of amides.

According to the present invention an amide is formed by bringing an oxime, in vapour phase, in contact with an acid-reacting catalyst.

Suitably the catalyst consists of a mixture of an acid, for example phosphoric acid, and a

solid support material, preferably a solid adsorbent.

Suitably the adsorbent is a silicious material. Suitable catalyst supports include diatomaceous earth, Kieselguhr and artificially prepared porous silica. Other suitable catalyst supports include aluminium silicates, for example, fullers earth, Bentonite and Montmorillonite.

Other acids which may be employed as catalyst, with or without a support, are silicomolybdic acid, and molybdic acid.

Other catalysts which may be employed include acid reacting salts.

Typical acid reaction salts are:  
(a) sodium hydrogen sulphate  
(b) cadmium hydrogen phosphates or cad-

25

30

35

55

60

65

mium copper hydrogen phosphates, for example, as described in British Patent Specification 460,659

5 (c) calcium copper hydrogen phosphate, for example, as described in British Patent Specification 535,062

(d) copper pyrophosphate catalysts, for example, as described in British Patent Specifications 518,749 or 521,891.

10 (e) Friedel-Crafts catalysts.

Other catalysts which may be employed include refractory metal oxide cracking catalysts such as silica/alumina and silica/magnesia.

15 A preferred class of compound for treatment in accordance with this invention consists of the cycloalkanone oximes. By the use as feedstock of cyclohexanone oxime there is obtained caprolactam.

20 Other compounds which may be treated according to this invention are dialkyl ketoximes, diaryl ketoximes and alkylaryl ketoximes, alkyl aldoximes and aryl aldoximes.

25 Usually reaction temperatures will lie in the range 200—500°C. Pressure may be atmospheric; if desired lower or higher pressure may be employed. When using cyclohexanone oxime as feedstock a temperature in the range 200—250°C has been found suitable at a

pressure in the range 2—20 cms pressure of 30 mercury.

If desired the oxime may be passed over the catalyst as a mixture with an inert gaseous phase diluent.

35 The oxime may be used in admixture with a polymerisation inhibitor in order to reduce side reactions involving polymerisation of the amide.

This invention is illustrated but not limited by the following Example.

40 EXAMPLE.

Eight grams of pure cyclohexanone oxime was vaporised, at 150°C and reduced pressure, in a stream of nitrogen and the mixture passed upward through a vertical glass tube packed with 20 grams of a phosphoric acid-on-Kieselguhr catalyst. This catalyst was heat treated before use at 200°C. for one hour.

45 The catalyst bed was maintained at 230°C by means of an electric heater and product condensed by means of an air cooled condenser. Pressure in the system beyond the catalyst bed was 20 mm of mercury.

The product was recrystallised by means of petroleum ether, yield being 48% by weight of 50 pure caprolactam (m.p. 68°C).

55 J. WOOLARD,  
Agent for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1961.  
Published by The Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.